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# THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

## XXVI. THE EFFECT OF FLOW CONFIGURATION ON THE OXIDATION AND IGNITION OF HYDROGEN IN MIXTURES WITH AIR SUPPLIED TO VERTICAL COMBUSTION TUBES OF VARIOUS MATERIALS[1]

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### ABSTRACT

Experiments to determine the effect of flow configuration on the oxidation and ignition of hydrogen in mixtures with air, described in this Part, are the second of a new series carried out with a method described in Part XXIII and used for experiments with acetaldehyde and pentane. Oxidation and ignition of hydrogen in mixtures with air occurred solely on the surface of the combustion tube. The wall temperature required for ignition, as measured on the outer surface, exceeded a minimum of 500°C. to an extent increasing with increases in hydrogen concentration, with increases in the catalytic activity of the tube surface, and with decreases in the rate of mixture supply if that rate were lower than the value required for turbulent flow. The effect of these factors depended to a remarkable degree on whether flow configuration was due to the convection circulations which existed at relatively low rates of mixture supply or to the turbulence accompanying greatly increased rates. When, for example, a mixture containing 50% of hydrogen was supplied to combustion tubes of silica and of stainless steel with an aged surface, at 200 cc./min. the surface temperatures required for ignition were 600° and 790°C. respectively. When, however, the rate of supply was increased to 1000 cc./min. and flow configuration became turbulent, ignition temperatures were in the same order but the total difference was 30°C. and diminished to approximately 15°C. only, as rate of mixture supply was further increased to 2500 cc./min. The increase in ignition temperatures, as measured on the outer surface of the combustion tubes, that always occurred after turbulence had been established and rate of mixture supply further increased was probably due to the increase in the rate of heat transfer required to maintain the inner surface at an igniting temperature. It was found by associated experiments that the premature ignition commonly obtained when hydrogen is used as the fuel for an Otto cycle engine is, in accordance with the experiments of this Part, due to an igniting temperature having been attained by the exhaust valve or the ceramic core of the spark plug. The engine experiments will be described in the next of the present series of papers.


### INTRODUCTION

The combustion tube method used for experiments made to determine the effect of flow configuration on the oxidation and ignition of acetaldehyde and *n*-pentane in mixtures with air, described in Part XXIII (9), was again used for experiments with the hydrogen–air mixtures of this Part. It was shown by the experiments with acetaldehyde and pentane that ignition occurred at two temperature levels if the combustion tube was of silica but not if it was of steel.

When a chemically correct acetaldehyde–air mixture was supplied to the silica tube at 100 cc./min. the first igniting effect occurred when the maximum

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temperature of the wall, as measured on the outer surface, was 260°C. The second ignition occurred at a maximum wall temperature of 679°C. When a "correct" *pentane–air mixture* was supplied at the same rate, the first and second igniting temperatures were 321° and 574°C. respectively.

The first igniting effect was in both cases preceded and followed by cool flames which caused pressure fluctuations as they traversed the mixture. They disappeared before the occurrence of the second igniting effect. The temperature of the first ignition varied little with change of mixture strength or as rate of mixture supply was increased.

The temperature of the second igniting effect diminished rapidly as mixture strength was increased from weak to correct or as rate of mixture supply was increased from 100 cc./min. It was found also that the second igniting effect was not a consequence of the first. That is, the effects were not related and the characteristics of the second indicated that it occurred on the wall of the tube.

The first igniting effect, when obtained with the usual methods of experiment, is generally attributed to a chain reaction and mistakenly as preliminary to the second. The experiments mentioned above indicated however that the first ignition occurred when material nuclei were present in the reacting mixture. Thus it was evident that formaldehyde was formed by the partial oxidation of *n*-pentane or acetaldehyde on the wall of the tube at the temperatures of the first igniting effects. The formaldehyde was necessarily carried into the mixture ascending the tube by circulating convection currents. It is assumed that condensation products and the sudden decomposition of organic peroxide, if then formed, would provide the nuclei required for ignition. This hypothesis was supported by the results of engine experiments on the compression ignition of mixtures with air of acetaldehyde and of *n*-paraffins (7, 5, 8, 6).

Hydrogen cannot provide material nuclei of ignition in the manner described. The characteristics of its combustion and ignition in vertical combustion tubes and in engines are therefore of exceptional interest. The former are described in this Part; the latter are to be described in the next of the series.

A hydrogen–air mixture is always turbulent after admission to an engine cylinder. Combustion tube experiments with flow configuration dependent on turbulence as well as on heat convection are therefore described in this Part.

### I. THE FLOW CONFIGURATION DUE TO HEAT CONVECTION IN VERTICAL COMBUSTION TUBES WITH TEMPERATURE GRADIENTS

#### *Experimental Arrangements*

The diagram of Fig. 1 was drawn with the horizontal scale double that of the vertical. It shows a combustion tube supported concentrically in a tubular electric furnace, and the ends of the annulus between the heated wall of the furnace and the tube closed by transite washers. The heated length of the furnace was 6½ in. and the combustion tube projected three inches from its ends. The temperature gradients over the length within the furnace were determined by using a slidable wire ring of chromel and alumel with diametrically opposite junctions. A precision potentiometer was used to balance

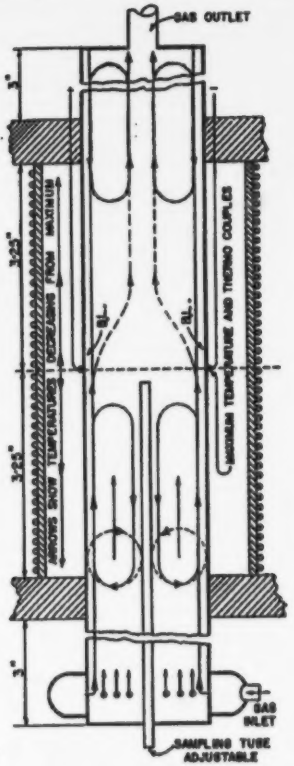


FIG. 1. Diagram showing the arrangement of a combustion tube concentrically in an electric furnace, the position of measurement of the apparent ignition temperature, the method of admitting gaseous mixtures, the convection circulations with non-turbulent gas flow, and the axis sampling device.

the thermoelectric potential against a standard cell. The equilibrium temperature gradients thus measured along a stainless steel tube, 28 mm. internal diameter and 1.58 mm. wall thickness, supported in a 2 in. diameter furnace are shown by the graphs of Fig. 2 for rates of heat input to the furnace varying from 135 to 344 watts; air or nitrogen was supplied at 200 cc./min. The graphs show that maximum wall temperature of the stainless steel tube was always attained at approximately the midsection of the tube length within the furnace. The position of maximum temperature was approximately half an inch above the midsection when the tube was of silica.



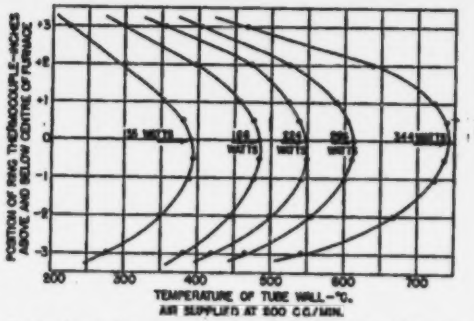


FIG. 2. Graphs showing surface temperature gradients from the midsection of the tube to the cool ends.

Hydrogen–air mixtures were admitted to the lower end of the combustion tube through a ring of holes in the periphery of a distributor type of inlet. When a mixture was supplied at rates commonly used for combustion experiments it tended to ascend along the heated wall of the tube and flow configuration depended on heat convection. The direction of flow through the distributor holes was however normal to the longitudinal axis of the tube and it was thus possible by increasing rate of mixture supply to create turbulence in the mixture passing through the tube while its space velocity was far less than would be required to exceed the critical Reynolds Number.

*Flow Configuration Due to Heat Convection*

An outline of the flow configuration in a transparent combustion tube when nitrogen was supplied through the distributor inlet at 100 cc./min. and the maximum wall temperature maintained at 500°C. was made visible by the method described in Part XXIII (9, p. 105). This outline, as shown by the solid flow lines of the diagram, Fig. 1, comprised a lower convection circulation extending over the rising temperature gradient below the midsection of the length of tube within the furnace and a shorter upper circulation over the falling temperature gradient above the midsection. The circulations are separated from actual contact with the tube wall by a boundary layer (B.L.) moving relatively slowly. The temperature of the mixture in the lower circulation is raised by heat from the wall, transmitted through the boundary layer. The mixture in the upper circulation, which passes over a falling temperature gradient, loses heat by transmission through the boundary layer to the wall before leaving the upper end of the tube. Thus its direction of motion was seen to be opposite to that of the lower circulation.

It was not possible to observe the pattern of flow within the convection circulations nor in the space between them. That within the lower circulation determines rate of heat transfer from the boundary layer to the mixture passing through the tube and the rate of reaction of the electrolytic gas in the

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mixture as it ascends the tube. The ascending stream of this circulation receives initially all of the mixture supplied to the tube at rates which permit its existence. Its space velocity must therefore be higher than that of the descending stream in the constant pressure conditions of the experiments and also because temperature is raised continuously as it passes up the tube. It would be expected from considerations of gas dynamics that flow configuration within the circulation would comprise a procession of toroidal vortices moving upwardly with the mean space velocity of the mixture. A single vortex is shown in cross section by broken line circles, Fig. 1, and its upward movement indicated by arrows. The vortex is shown as penetrating the boundary layer. The thickness of the layer is shown to remain unchanged over the length of the combustion tube. The thickness would however diminish as penetration by the vortices increased. The degree of penetration would depend on the tendency of the diameter of the vortices to increase as the rotational velocity about their horizontal axis increased. This in turn would vary with the difference in temperature between the ascending and descending streams of the convection circulation.

## II. TOROIDAL VORTICES AND RATES OF REACTION OF HYDROGEN–AIR MIXTURES ASCENDING A VERTICAL COMBUSTION TUBE OF STAINLESS STEEL

The procession of vortices ascending the rising temperature gradient of the lower convection circulation removes heated gas from the boundary layer and replaces it with cooler gas from the descending central stream. The rate of surface reaction as the hydrogen–air mixture passed up the tube could then be measured by the analysis of samples taken at points along the vertical axis. Experiments were carried out accordingly with the mixtures supplied to the stainless steel combustion tube at the relatively low rates required for the formation of convection circulations rather than general turbulence. The tube was 28 mm. internal diameter. The wall was 1/16 in. thick. The vertically adjustable sampling tube is shown by Fig. 1. It was of silica, 1/8 in. diameter and 1/16 in. bore. It is considered that samples remained unaltered while being drawn through the tube. Hydrogen was used in various concentrations in mixtures with air and corresponding concentrations of electrolytic gas, $2H_2+O_2$, are given by the graphs of Fig. 3. Electrolytic hydrogen, as supplied

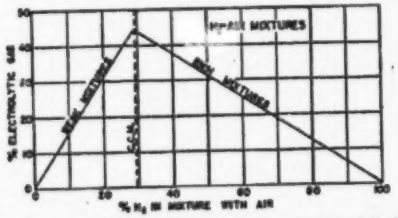


FIG. 3. Graph showing the relation between the concentration of hydrogen in a mixture with air and that of the electrolytic gas in the mixture.



by the Canadian Liquid Air Company, compressed to 2000 lb./sq. in. in steel cylinders, was used for the experiments. It was purified of oxygen before compression. It was then 99.95% hydrogen and nearly dry, the dew point being below minus 100°F. Experimental results are given by the graphs of Figs. 4, 5, and 6, and are described below in related paragraphs.

*Fig. 4, Maximum Wall Temperature 550°C., Hydrogen Concentration 49%, Electrolytic Gas 32%, Mixture Supplied at 100 cc./min.*

It is shown by Fig. 4 that reaction of the 32% of electrolytic gas in the mixture with air containing 49% of hydrogen began at approximately 3 in. below the midsection. That position is 0.25 in. within the furnace, and wall temperature would be 425°C. according to the relevant graph of Fig. 2. The

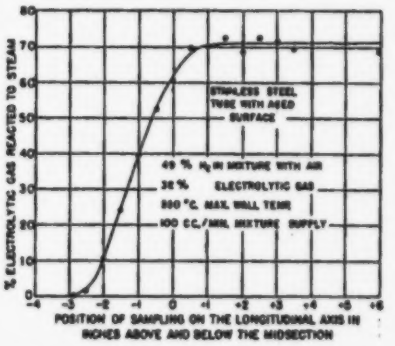
% ELECTROLYTIC GAS REACTED TO STEAM
STAINLESS STEEL TUBE WITH AGED SURFACE
49 % H₂ IN MIXTURE WITH AIR
32 % ELECTROLYTIC GAS
550 °C. MAX. WALL TEMP.
100 CC./MIN. MIXTURE SUPPLY
POSITION OF SAMPLING ON THE LONGITUDINAL AXIS IN INCHES ABOVE AND BELOW THE MIDSECTION

FIG. 4. Rate of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature 550°C., and 49% of hydrogen in mixture with air, supplied at 100 cc./min.

graph of the figure shows that rate of reaction increased slowly at first and then rapidly with the result that 60% of the concentration of electrolytic gas was reacted in the length of tube below midsection, over which wall temperature had increased from 425° to 550°C. Wall temperature then diminished and rate of reaction decreased to become zero at 1.5 in. above the midsection. Of the electrolytic gas in the mixture supplied to the tube, 71% had then been reacted to steam.

*Fig. 5, Maximum Wall Temperature 755°C., Hydrogen Concentration 45%, Electrolytic Gas 34.6%, Mixture Supplied at 100 cc./min.*

The temperature gradient below the midsection of the length of stainless steel combustion tube within the furnace was determined and is shown by graph B of the figure. Rates of surface reaction are given by graph A. It will be noted that the temperature of the tube wall was 605°C. at 3.0 in. below the midsection, that is 0.25 in. within the furnace, and that 30% of the electrolytic gas in the mixture had previously been reacted. The rate of reaction became so great that 80% of the electrolytic gas had been reacted at a position 2.6 in.

below the midsection. That is, a further 50% of the electrolytic gas was reacted while the boundary layer passed over 0.4 in. length of tube wall; the corresponding increase in wall temperature being from 615° to 715°C. over this length, see graph B. The increase in the reaction rate then diminished as the boundary layer passed over a length of 2.1 in. before reaction of the electrolytic gas was

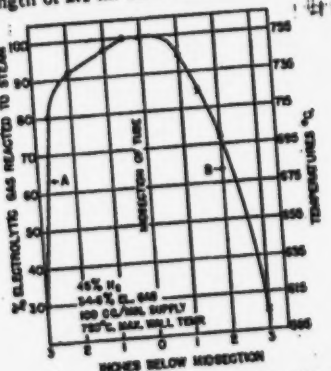


Fig. 5. Graph A. Rate of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature 750°C., 45% of hydrogen in mixture with air supplied at 100 cc./min.
Graph B. Temperature gradient on wall from midsection to 3 in. below that position.

100% complete at 0.5 in. below the midsection, which was at a temperature of 755°C. It will be seen by comparing graphs A and B that rate of reaction was generally similar to rate of increase of wall temperature.

*Fig. 6, Maximum Wall Temperature 585°C., Differing Hydrogen Concentrations, Mixtures Supplied at 200 cc./min.*

In addition to an experiment with a correct mixture, others were made with mixtures containing hydrogen in concentrations of 19 and 52%. These will be described as "weak" and "rich", and each contained 30% of electrolytic gas. Experimental results for rates of reaction are given by the graphs of Fig. 6.

The remarkable increase in rate of reaction that occurred on increasing the hydrogen concentration from 19 to 52% is shown by a comparison of Graphs A and B of the figure.

Reaction of the rich mixture began at 1.5 in. below the midsection of the tube and increased with such rapidity that 79% of the electrolytic gas had been reacted to steam at 2.0 in. above the midsection. There was no appreciable reaction between that position and the tube outlet. Reaction of the weak mixture began at a position one half inch closer to the midsection and 25% only of the electrolytic gas had been reacted at 2.0 in. above the position. There was no further reaction. The especially significant feature is that at the midsection of the tube where wall temperature had attained a maximum value



of 585°C., 42% of the electrolytic gas in the rich mixture had been reacted and 11% only of that in the weak mixture. As each contained 30% of electrolytic gas when supplied to the tube, this means that at the position of maximum wall temperature where ignition is generally assumed to occur, the rich mixture contained 17.4% and the weak mixture 26.7% of electrolytic gas. Inflammability and the surface temperature required for ignition would vary accordingly.

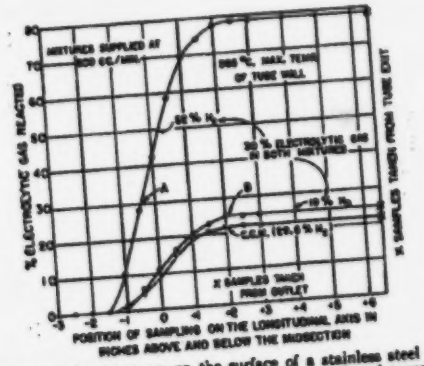
% ELECTROLYTIC GAS REACTED
% SAMPLES TAKEN FROM TUBE EXIT
A
B
POSITION OF SAMPLING ON THE LONGITUDINAL AXIS IN INCHES ABOVE AND BELOW THE MIDSECTION

Fig. 6. Rates of reaction to steam on the surface of a stainless steel combustion tube. Maximum temperature 585°C.; 52, 19, and 29.6% of hydrogen in mixtures with air supplied at 200 cc./min.

A comparison of results for a chemically correct mixture with those for the mixture containing hydrogen in the concentration of 19% is of interest. The former contains hydrogen in the concentration of 29.6% and electrolytic gas in the concentration of 45%; the latter contains 30% of electrolytic gas. It is shown, however, by the relevant graphs of Fig. 6 that the rate of reaction of electrolytic gas was approximately 3% the greater for the mixture containing the smaller concentration of hydrogen.

## III. THE IGNITION OF HYDROGEN–AIR MIXTURES SUPPLIED AT 100 CC./MIN. TO COMBUSTION TUBES OF VARIOUS MATERIALS

The combustion tubes were of stainless steel, silica; sillimanite, and carbon. The steel tube was 1½ in. internal diameter and the others approximately 1.0 in. The wall of the carbon tube was 1/4 in. thick, that of the others 1/16 in. The tubes were arranged in a vertical electric furnace as shown by Fig. 1, with thermocouples set at the midsection of the length within the furnace in order to measure the maximum temperature attained by the wall. The object of the experiments was to determine the temperature at that position when ignition occurred. Thus an approximate temperature having been obtained, the tube was allowed to cool until the temperature fell from 30° to 40°C. It was then reheated very slowly until ignition occurred again. Ignition temperatures thus

measured at the midsection of the tube must, according to the experiments of Section II, be higher than real values to an extent which varies with the degree of surface activity, with the concentration of hydrogen in excess of that required for a correct mixture, and with the time of contact of the mixture with the surface below the midsection, at a temperature such that reaction of electrolytic gas to steam can occur. The measured igniting temperatures will therefore be described as *"apparent ignition temperatures"* and the term abbreviated to A.I.T.

*The Silica Tube*

It is shown by Graph A, Fig. 7, that the A.I.T. was substantially constant with hydrogen concentration diminishing from 30 to 20%. Then as the concentration was further reduced to 8% and the concentration of excess oxygen increased accordingly, the increase in A.I.T. was 3°C. only. When however hydrogen concentration was *increased* from 30 to 80%, the A.I.T. rose slowly

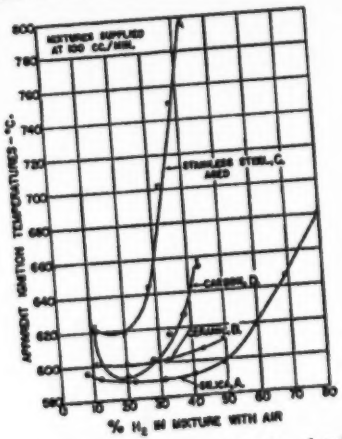


FIG. 7. Apparent ignition temperatures, combustion tubes of various materials, hydrogen concentration increasing from 10% in mixtures with air supplied at 100 cc./min.

at first and then rapidly to a value of 680°C. The concentration of electrolytic gas was approximately 12½% in mixtures containing either 8 or 80% of hydrogen, but the values for A.I.T. were 595° and 680°C. respectively. This result, obtained with a low rate of mixture supply and what is reputed to be a stable surface of minimum activity, illustrated the rise in A.I.T. due to the increase in rate of reaction below the midsection of the tube that is obtained as hydrogen concentration is increased.

*The Sillimanite (Ceramic) Tube*

The material was reputed to be a mixture of 62% alumina, 35% silica, and 3% oxides of other metals. The tube was used for the purpose of demonstrating the effect of spark plug cores of similar material in igniting hydrogen–air mixtures in an engine. Values for A.I.T. were determined accordingly for mixtures with air containing hydrogen in concentrations ranging from 10 to 50%. This is equivalent to mixtures ranging from 75% weak to 140% rich, as used in an engine, Graphs A and B show that values obtained for A.I.T. varied in the same manner for sillimanite and silica but that those for sillimanite were approximately 10°C. the higher.



*The Stainless Steel Tube, Aged Surface*

The tube had been used for experiments described in Section II. The surface had become oxidized and is therefore described as "aged". It will be seen by Graph C of Fig. 7 that a minimum of 620°C. was observed for the A.I.T. when the mixture with air contained hydrogen in the concentration of 20% and that a slight rise in A.I.T. occurred on reducing the concentration to 10%. However on increasing the hydrogen concentration, values for A.I.T. increased so rapidly that with 42% of hydrogen in the mixture, ignition was not obtained until the midsection was heated to 828°C.; not shown, Fig. 7. This ignition must therefore have occurred in the tube below the midsection of maximum temperature. This result is as would be expected from the experimental results shown by Fig. 5. These were obtained with the same combustion tube and the same rate of mixture supply, and all of the electrolytic gas in a mixture containing 45% of hydrogen was reacted to steam below a midsection temperature of 755°C.

*The Carbon Tube*

It will be seen by reference to Graph D of Fig. 7 that a minimum value of 592°C. was obtained for the midsection temperature required for the ignition of a hydrogen–air mixture in the carbon tube. The mixture then contained hydrogen in the concentration of 20% and the ignition temperature was approximately that obtained with the silica tube and the same concentration of hydrogen. Carbon tube ignition temperatures unlike those obtained for the silica tube rose rapidly as the concentration of hydrogen was either increased or diminished and ignition temperatures of 620° and 627°C. were obtained with hydrogen concentration of 10 and 38% respectively. On increasing the hydrogen concentration to 42% a temperature higher than 654°C. was required for ignition. The carbon surface was then glowing brightly and values for ignition temperatures were not obtainable.

It was found however that the carbon and graphite tubes used for the experiments were in some degree transparent to hydrogen. It is probable therefore that the rise in A.I.T. that occurred on increasing hydrogen concentration was affected accordingly.

The experimental results are however of significance, because it was shown by those given in Part XXIII (9, p. 108) that mixtures of air with pentane or acetaldehyde were not ignited in the carbon tube or in a graphite tube although the midsection temperature was raised to 760°C.

## IV. IGNITION TEMPERATURES AS AFFECTED BY SURFACE STATE AND COMBUSTION TUBE MATERIAL, FLOW CONFIGURATION BEING DEPENDENT ON HEAT CONVECTION

Difficulties have been encountered in the obtaining of repeatable values for A.I.T. of hydrogen–air mixtures, especially when the steel combustion tubes are used, and rates of supply are such that flow configuration is governed by heat convection. The difficulties are due to changes in surface state that occur in the course of a series of experiments for which hydrogen concentration is varied. The extent to which observed values are not repeatable increases as hydrogen concentration increases.

Numerous methods of surface treatment were tried in attempts to obtain repeatable values for A.I.T. The methods, in addition to those commonly applied to vitreous surfaces, included the reduction of surface oxide by long exposure to hydrogen while the midsection of the tube was maintained at 680°C. as well as the formation of surface oxide by a similar treatment with oxygen. Nearly repeatable, but relatively low values for A.I.T. were obtained if, before beginning experiments with a stainless steel tube, the surface were cleaned by the usual method of pickling with a hot 10% solution of hydrochloric acid in water. Nearly repeatable but relatively high values for A.I.T. were obtained if the stainless steel surface were aged by continuous use after a coating of oxide had been formed. The "activity" of the surface thus formed was responsible for the relatively high values for A.I.T. obtained when hydrogen was in excess of the concentration required for a correct mixture with air. The activity of the surface diminished during a period of disuse and a period of reuse was required to regain repeatable values for A.I.T.

### *Values for A.I.T., Aged and Clean Stainless Steel Tubes*

Mixtures containing hydrogen in concentrations rising from 10% were supplied to the tubes at rates of 200 cc./min. Experimental results are given by Fig. 8.

Graph A of the figure shows the values obtained for A.I.T. when the mixtures were supplied to the aged stainless steel tube. This tube had been used for the experiments described in Sections II and III.

Graph B shows the results obtained when a similar stainless steel tube was used after the surface had been cleaned by the pickling method. The experimental results for the similar tubes with different varieties of surfaces show differences in values of A.I.T. increasing to a remarkable extent as hydrogen concentration in the mixture supply was increased. Thus when a correct mixture was supplied, the values for A.I.T. were 640° and 610°C. for the aged and clean tubes respectively. When the hydrogen concentration was 40% the respective values for A.I.T. were 745° and 615°C. and 790° and 635°C. when hydrogen concentration was 50%. Values for A.I.T. were not obtainable below 800°C. when the mixture supplied to the aged tube contained hydrogen in greater concentration than 52% but were obtained for concentrations increasing to 80% in mixtures supplied to the clean tube.

Values for A.I.T. lying between those shown by the graphs of Fig. 8 were



obtained after various other methods of treatment had been used but were not repeatable. Pretreatment of the aged surface with hydrogen led to higher values being obtained for A.I.T. when oxygen was in excess in the mixtures supplied, but the values were not repeatable.

Graph A of Fig. 8 may be taken to represent the upper limit of repeatable values for A.I.T. and Graph B, the lower.

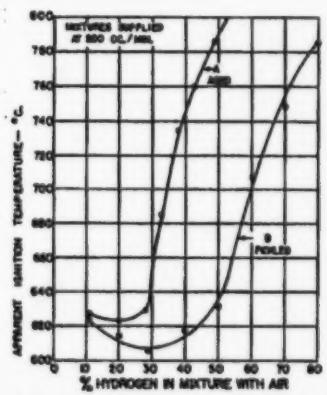


FIG. 8. Apparent ignition temperature as affected by the surface state of a stainless steel combustion tube. Hydrogen concentration increasing from 10% in mixtures with air, supplied at 200 cc./min.

### *Values for A.I.T. Mild and Stainless Steel and Silica Tubes*

The mild steel tube was cleaned by pickling before being used. The silica surface was not treated in any way. The hydrogen–air mixtures were supplied at 200 cc./min. and an additional experiment with the silica tube was carried out with mixtures supplied at 100 cc./min. The experimental results are shown by Graphs A, C, and D of Fig. 9. Graph B for the clean stainless steel tube is reproduced from Fig. 8.

The surface of the mild steel tube oxidized rapidly and tended to pit and scale. It will be seen, Graph A, that a minimum of 650°C. was obtained for the A.I.T. with a hydrogen concentration of 20%. The values then increased so rapidly as the concentration of hydrogen was increased or diminished that A.I.T. values less than 800°C. were not obtained with a hydrogen concentration greater than 33%, or less than 700°C. when the concentration was less than 10%. Graph C, obtained for the silica tube with mixtures supplied at 100 cc./min., follows the pattern of Graph B for the stainless steel tube and the A.I.T. for a correct mixture was lower by 10° only. Moreover the values for A.I.T. varied little for hydrogen concentrations ranging from 10 to 40%. An especially significant result is the relatively rapid rise in A.I.T. obtained as

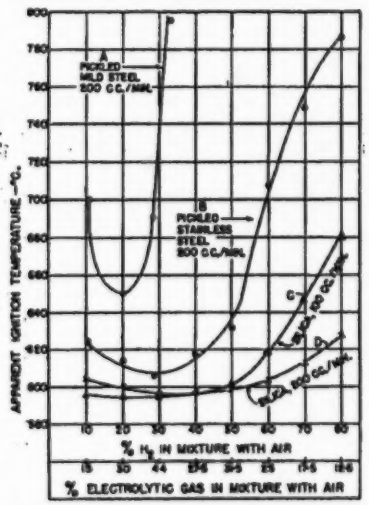
A PICKLED MILD STEEL 200 CC./MIN.
B PICKLED STAINLESS STEEL 200 CC./MIN.
C SILICA 100 CC./MIN.
D SILICA 200 CC./MIN.
APPARENT IGNITION TEMPERATURE—°C.
% $H_2$ IN MIXTURE WITH AIR
% ELECTROLYTIC GAS IN MIXTURE WITH AIR

FIG. 9. Apparent ignition temperatures, hydrogen increasing in concentrations from 10% in mixtures with air supplied to combustion tubes of mild steel, stainless steel, and silica at 200 cc./min. and to the silica tube at 100 cc./min.

hydrogen concentration was increased from 40 to 80% in the mixture supplied at 100 cc./min. as compared with that obtained over the same range of hydrogen concentration when the mixtures were supplied at 200 cc./min. as shown by Graph D.

## V. APPARENT IGNITION TEMPERATURES AS AFFECTED BY REPLACING CONVECTION CURRENTS WITH TURBULENCE

The design of the distributor inlet used for admitting hydrogen–air mixtures to the lower ends of vertical combustion tubes was described in Section I and illustrated by Fig. 1. It is such that turbulence tends to be created in the mixture as admitted, on increasing the rate of supply. A "stilling" length of tube was not provided and initial turbulence would persist as the gaseous mixture passed upwardly through combustion tubes of the length and diameter used for the experiments of this Part. Thus, turbulence, after being initiated by increasing rate of mixture supply to the requisite value, would increase as rate continued to be increased although the Reynolds Number, even at the highest rate used for experiments, was far below the critical value. The effect on flow configuration would be that circulating convection currents would tend to be replaced by turbulence when rate of mixture supply exceeded a value which can be determined by experiment only. Experiments carried out accordingly are described in this Section.



### *Stainless Steel Tube with Clean Surface*

The changes in the relation between A.I.T. and hydrogen concentration that occurred as the mixture supply was increased from 60 to 2000 cc./min. are shown by the family of graphs, Fig. 10. It will be seen that they fall into two groups of plainly different characteristics.

The first group comprises the graphs for values of A.I.T. obtained when mixtures were supplied at 60 to 400 cc./min. Definite minimum values for A.I.T. differing little from 608°C. were then obtained when the mixture was approximately correct. Values of A.I.T. increased rapidly with increasing concentrations of hydrogen. The rate of increase diminished as rate of supply was increased to 400 cc./min. Thus for example when the concentration of hydrogen in the mixture was 50%, the A.I.T. was 755°C. with a rate of supply of 60 cc./min. and 630°C. with a rate of 400 cc./min. It is indicated by the experimental results and those described earlier in this Part that circulating convection currents persisted in the mixture passing through the tube until rate of supply was increased to at least 400 cc./min.

The second group comprises the graphs for values of A.I.T. observed when mixtures were supplied at rates of from 700 to 2000 cc./min. It will be seen that the increase in rate of supply of from 400 to 700 cc./min. was accompanied by an increase in the minimum value of A.I.T. from 608° to 622°C. Moreover, the higher value instead of increasing with an increase in hydrogen concentration, remained substantially constant over the hydrogen concentration range of 30 to 50%. The minimum value for A.I.T. continued to increase with increases in the rate of mixture supply and as this occurred it extended over an increasing range of hydrogen concentration. Finally when rate of supply had been increased to 2000 cc./min., a minimum value for A.I.T. of 650±2°C. was obtained for hydrogen concentrations ranging from 30 to 80%.

As the concentration of hydrogen was decreased from 30 to 10%, values of A.I.T. increased at nearly similar rates as the rate of mixture supply was increased from 700 to 2000 cc./min. The total increase was 15°C. with mixtures supplied at 700 or 1000 cc./min. and 20°C. at a rate of 1500 or 2000 cc./min.

The radical change in ignition characteristics that occurred on increasing rate of mixture supply from 400 to 700 cc./min. is attributed to circulating convection currents having been displaced by turbulence.

### *Experiments with Correct Hydrogen–Air Mixtures Supplied at 50 to 2500 cc./Min. to Silica and Clean Stainless Steel Tubes*

The values obtained for apparent ignition temperatures as rate of supply of a correct mixture was increased from 50 to 2500 cc./min. are given by the graphs of Fig. 11. It is shown by Graph B of the figure that when the combustion tube was of clean stainless steel, the relation between A.I.T. and rate of mixture supply follows closely that obtained in the earlier experiments with a similar tube as shown by the graphs of Fig. 10.

Experiments were not carried out earlier with a silica tube and rates of mixture supply greater than 200 cc./min. The A.I.T. at this rate as shown by

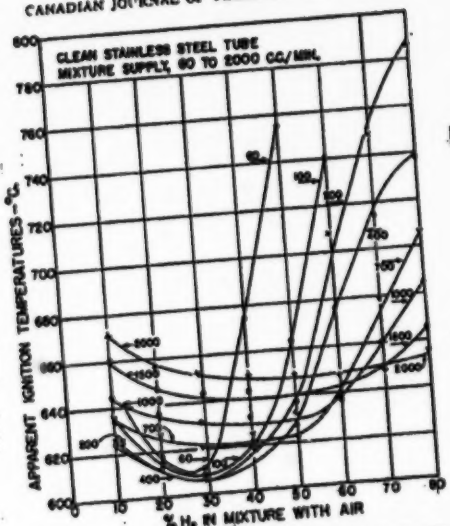


FIG. 10. The change in the characteristics of apparent ignition temperature obtained when, by increasing rate of mixture supply, the flow configuration due to heat convection is replaced by turbulence. Hydrogen concentrations ranging from 10 to 80% in mixtures with air supplied to a stainless steel combustion tube at 50 to 2000 cc./min.

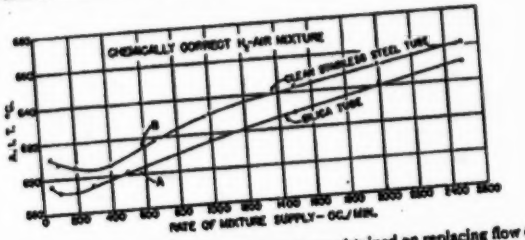


FIG. 11. The effects on apparent ignition temperatures obtained on replacing flow configuration due to heat convection by that due to turbulence, correct hydrogen–air mixtures supplied to silica and stainless steel combustion tubes at 50 to 2000 cc./min.

Graph A of Fig. 11 was 590°C. It was 604°C. with the clean stainless steel tube, Graph B of the figure. The respective values obtained earlier, as shown by Fig. D, were 596° and 607°C. The consistency is as good as would be expected in view of small changes in surface state which cannot be avoided. The significant feature of the experiments is that when a *correct* mixture was supplied to the combustion tubes, the difference between values obtained for A.I.T. varied little as circulating convection currents were replaced by turbulence.



*Experiments with Mixtures Containing 50% of Hydrogen Supplied at 50 to 2500 cc./Min. to Silica and to Stainless Steel Tubes, Clean, and Aged*

It was shown by the experimental results, Fig. 10, obtained when a clean stainless steel tube was used, that circulating convection currents tended to be replaced by turbulence as the rate of mixture supply exceeded 400 cc./min. and that the transition had been completed when the rate was 700 cc./min. These results, obtained with one variety of surface, do not illustrate the corresponding effect on rate of reaction, and the consequent value of A.I.T., of other more or less active surfaces when hydrogen concentration is greater than required for a correct mixture. Surfaces in order of increasing activity are provided by combustion tubes of silica, stainless steel with a clean and with an aged surface. Values obtained for A.I.T. when using these tubes and a mixture with air containing 50% of hydrogen are given by the graphs of Fig. 12. They show that when flow configuration was due to heat convection, the

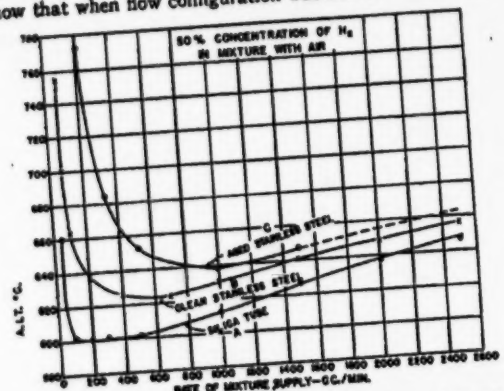


FIG. 12. The effects on apparent ignition temperature obtained on replacing flow configuration due to heat convection by that due to turbulence. 50% of hydrogen in mixtures with air supplied at 50 to 2500 cc./min. to a silica tube and to a stainless steel tube with a clean and with an aged surface.

values of A.I.T. and the extreme difference between them, which was dependent on the degree of surface activity, decreased rapidly as mixture supply was increased and time of residence diminished, and that after turbulence had been established, the values *increased* slowly and differences due to the degree of surface activity tended to disappear. Thus values of A.I.T. began to rise at rates of mixture supply of 400, 600, and 1000 cc./min. when the tubes used were of silica, and of stainless steel with a clean and with an aged surface, respectively. The over-all difference in the values of A.I.T. of nearly 180°C., which was obtained with a mixture supply of 200 cc./min., diminished to 37°C. on increasing the rate to 700 cc./min. and to 18°C. as it was further increased to 2500 cc./min. Thus surface activity, which was a predominant factor in

respect of the values obtained for A.I.T. when mixtures containing excess hydrogen were supplied at relatively low rates, became of very secondary importance when convection circulations were replaced by turbulence.

Apparent Ignition Temperatures were, as explained earlier, measured by thermocouples on the outer surface of a combustion tube at the position of maximum temperature. The effective temperature is that on the inner surface at the same position. This temperature has been found to be the lower by 10° or 12°C., at small rates of mixture supply. The difference would be expected to increase as rate of supply of turbulent mixture increased. This effect and the drop in temperature of the gas passing through a combustion tube when the area of heated surface remains nearly constant while the velocity of the gas flow increases may account for the rise in values of A.I.T. that occurred after turbulence became established.

## VI. PEROXIDES

Numerous attempts were made to detect hydrogen peroxide by titration of an aliquot of the liquid reaction product as trapped in condensers cooled with a dry ice – acetone mixture. Peroxide was not detected in the product from either the silica or the steel combustion tube when a 0.02 *N* potassium permanganate solution in water was used for the titration. It may be concluded that peroxide was not formed when reaction occurred in the flow configuration conditions of the experiments or, if formed, decomposition must have occurred before the mixture left the combustion tube.

## DISCUSSION

Many attempts have been made to show that mixtures of hydrogen with air or oxygen can be ignited apart from surfaces, by the application of heat. A comprehensive description of the methods tried and the results obtained is given by Jost (4, pp. 3–40). It appears accordingly that flow configuration has not been regarded as a determining factor in respect of the temperatures required for ignition. Dixon (2), for example, when using his concentric tube method, sought to avoid the wall effect by increasing the diameter of the outer tube which was heated electrically. He does not seem to have realized that by injecting the hydrogen through a small orifice in the end of the inner tube which projected halfway up the length of the outer one, a contra flow was set up which would bring reacting mixture into contact with its surface. It appears therefore that ignition occurred when the surface of the inner tube attained the necessary temperature and that the observed delay periods represented merely the times required.

Alyea and Haber (1) used the crossed streams method of determining the ignition temperature of mixtures of hydrogen and oxygen. The tubes carrying the heated gases to orifices in their ends were apparently far enough apart to prevent recirculation around them of a mixture of the gases. In these conditions no ignition occurred at reduced pressures of from 10 to 200 mm. Hg at temperatures up to 540°C. if pressure were gradually reduced so that what is generally regarded as the normal explosion region was entered. When however a surface of quartz, porcelain, or glass was placed at the junction of the crossing streams, an ignition always occurred when the explosion region was approached or entered.



Goldmann (3) using normal pressure and higher temperatures found that ignition occurred when one or other of the streams of hydrogen and oxygen was heated to 560°C. or higher. It was concluded that formation of active atoms or radicals producing a chain reaction leading to ignition was possible in the gas phase at temperatures above 560°C. but that at lower temperatures and pressures a surface was necessary for their production. The streams of gases issued from orifice tubes only a few millimeters apart and, in the light of the flow configuration experiments described in this Part, it is probable that a mixture of the reacting gases circulated about the tube carrying the heated gas. Thus it is possible that ignition as observed by Goldmann was a surface effect instead of one occurring in the gas phase.

*Flow Configuration Due to Heat Convection in a Vertical Combustion Tube*

The mixture supplied to the lower end of the tube forms a convection circulation over the lower temperature gradient and is separated from the wall by the boundary layer. When however reaction occurs on the surface the reacted mixture containing steam diffuses through the boundary layer to join the ascending stream of the convection circulation and is replaced by less reacted mixture diffusing through the boundary layer in the opposite direction. The normally laminar flow in the boundary layer is disturbed accordingly. The rate of surface reaction at a particular position on the tube surface will be governed in the circumstances by its temperature, the nature of the surface, and the rates of diffusion which would in turn depend on the thickness of the boundary layer, its density, and the density of the mixtures diffusing through it. The densities would diminish on increasing the concentration of steam in the mixture with air. The concentration of steam in the mixture at the position of maximum temperature would then depend on the factors mentioned and rate of supply of unreacted mixture to the tube.

If the oppositely moving streams of the lower circulation form toroidal vortices instead of remaining intact, all of the effects mentioned would increase in magnitude; rates of diffusion especially would increase because of the tendency of the vortices to expand and thereby reduce the thickness of the boundary layer. Its thickness has been shown by Fig. 1 as uniform but in reality it would increase or diminish as the vortices contracted or expanded according to temperature difference between the oppositely moving streams of the convection circulation.

The consequent effect of the factors described above on rates of reaction is shown by experiments described in Section II. For example, when a mixture containing hydrogen in a concentration of 45% was supplied to a stainless steel tube with an aged surface at 100 cc./min. while the midsection was maintained at 775°C., all of the electrolytic gas in it was reacted to steam in the length of tube below the midsection. The effect of excess hydrogen is again illustrated by a comparison of the rates of reaction obtained when mixtures

containing 19 and 52% of hydrogen were supplied to the tube at 200 cc./min. while the midsection temperature was maintained at 585°C. Both mixtures contained 30% of electrolytic gas but, as shown by the graphs of Fig. 6, 11% was reacted when the mixture contained excess oxygen and 42% when the mixture contained excess hydrogen. Conditions were similar in both cases except that, as supplied to the tube, the density of the mixture containing excess oxygen was 60% the greater. Secondary effects which are difficult to evaluate were the more rapid formation of steam in the mixture containing excess hydrogen and the smaller effect of the vortices in the less dense mixture to penetrate the boundary layer.

The relative rates of reaction in further experiments were taken to be indicated by the corresponding values of the A.I.T. It is of interest accordingly that when correct mixtures were used, the A.I.T. observed with a clean stainless steel tube to which the mixture was supplied at 200 cc./min. was approximately 10°C. only higher than when a similar mixture was supplied to a silica tube at either 100 or 200 cc./min., Fig. 9. The A.I.T. observed when the silica tube was used, if it had been measured on the inner wall, would differ little from the value of 585°C. assumed by Dixon to have been obtained apart from a surface (2). The rise in the values of A.I.T. as the concentration of hydrogen in mixtures supplied to the silica tube was increased is attributed to the decreasing density of the boundary layer and it will be noted that the rate of rise of A.I.T. increased on reducing the rate of mixture supply from 200 to 100 cc./min. as might be expected accordingly.

*Turbulence in the Combustion Tube and in the Combustion Chamber of an Engine*

The establishment of turbulence in the combustion tube was accompanied by a decrease in the thickness of the boundary layer and in the time of residence of the hydrogen–air mixture in the tube. There was therefore an increase in the rate of abstraction of heat from the inner surface of the tube and it became necessary to compensate for this effect by raising the temperature on the outer surface. Then because of the decrease in time of residence there was a diminution in the surface reaction of electrolytic gas to steam in the length of tube below the midsection; the variation in the amount of reaction due to differences in the nature of the tube surface also diminished. There was in consequence an increase in temperature required for ignition, as measured on the outer wall at the midsection, and a decrease in the effect of changes in the nature of the surface, on that temperature. There was then a corresponding decrease in the rise of the apparent ignition temperature that was observed in earlier experiments carried out at relatively low rates of supply of mixtures containing hydrogen in excess of the concentration required for a correct mixture. The combined effect of the factors mentioned increased as turbulence was increased on increasing rate of mixture supply, and thereby decreasing the time of residence in the tube. The result was that with a mixture supply of 2000 cc./min., the surface temperature required for ignition remained substantially constant while hydrogen concentration was increased from 30 to 80% and varied little with changes in the nature of the surface. The total difference due to changing



from a silica to an aged stainless steel surface was approximately 20°C. It was more than 200°C. when a mixture containing 50% of hydrogen was supplied at 200 cc./min. and flow configuration depended on heat convection.

Experiments with hydrogen–air mixtures supplied to an Otto cycle engine were carried on in association with the combustion tube experiments. Turbulence in both cases was increased by increasing the rate of mixture supply. This tended to reduce the temperature of the wall of the combustion tube but to *raise* the temperature of the wall of the combustion chamber of the engine, if it was operated at full throttle. The increase occurred because the increase in rate of mixture supply to the engine was obtained by increasing speed and consequently the heat load. The indirectly cooled surfaces of the exhaust valve and the ceramic core of the spark plug then tended to attain an igniting temperature in respect of the mixture as speed was raised in an attempt to develop maximum horsepower. The occurrence of premature ignition, in the circumstances, was avoided by a reduction in the exposed area of the ceramic core of the spark plug and by a reduction of the temperature of the exhaust valve, mainly by sodium cooling. The experiments will be described in the next of the present series of papers.

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